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MELT ADHESIVE CONTG. BLOCK CO-POLYMER + AGO OF VINYL-AROMATIC MONOMER AND  
BUTADIENE-ISOPRENE COPOLYMER BLOCK, GIVING HEAT-RESISTANT BOND

VINYL

FILMS  
LABELS

FLOOR AND WALL COVERINGS  
MEDICINAL PLASTERS

54 Melt adhesive on the basis of non-hydrated linear block  
copolymerisates A-B-A

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O.Z. 0050/034097

Patent Claims

1. A melt adhesive, basically consisting of a mixture of

A 100 % by parts of at least one non-hydrated linear block copolymerisate with the formula A-B-A that consists of

a1) end-located non-elastomeric polymer blocks A consisting of monovinyl-aromatic monomers,

a2) each of which having an average molecular weight of between 5,000 and 50,000 and

a3) representing a percentage content of between 10 and 50% by weight in relation to the linear block copolymerisate A-B-A and where

a4) B represents an elastomeric (co)-polymerisate consisting of butadiene and/or isoprene and in which case

a5) and furthermore the average molecular weight  $2A+B$  varies between 30,000 and 300,000;

B between 25 and 300% by weight of a resin with adhesive properties,

C between 5 and 200% by weight of a rubber diluent oil, if required,

D other commonly used additives in effective quantities,

characterized by the fact that the elastomeric (co)-polymerisate a4) contains butadiene and isopropene in a weight ratio of between 70:30 and 5:95.

2. A melt adhesive in accordance with claim 1, characterized by the fact that the monomers in the elastomeric copolymerisate a4) are distributed statistically.
3. A melt adhesive in accordance with claim 1, characterized by the fact that the elastomeric copolymerisate a4) has at least one lubricated transition between two polymerisate sequences, each of which contains a predominant percentage content of only one monomer.

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Melt adhesive on the basis of non-hydrated  
linear block copolymerisates A-B-A

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The invention concerns melt adhesives on the basis of non-hydrated linear block copolymerisates A-B-A with end-located polystyrene blocks A and an intermediately located part B, consisting of a mixed polymerisate of butadiene and isoprene with ratio ranging between 70:30 and 5:95 limits and in which the monomers are distributed in a random manner or in an arranged manner.

It is known that rubberlike block copolymerisates consisting of a monovinyl-aromatic compound (styrene) and a conjugated diene (butadiene or isoprene) may be used to manufacture melt adhesive mixtures. In addition to the block copolymerisates, these melt adhesive mixtures generally also contain one or more resins with adhesive properties such as colophonium derivatives, cumaron-indene resins and similar and a rubber diluent oil and, if required, anti-oxidants and other fillers (see (1) and (2)).

With respect to prior art, we refer to

- (1) DE-AS 15 94 254
- (2) DE-AS 20 11 036

It is known from (1) and (2) to use non-hydrated, linear, rubberlike three-block copolymerisates consisting of a monovinyl-aromatic compound and a conjugated diene in mixtures for adhesives. If, as described by the data given in (2), it is basically also possible to use mixed polymerisates as the component B, this document as well as (1) describe only linear block copolymerisates with an elastomeric center block B consisting only of butadiene or only of isoprene to be used for the manufacture of adhesive mixtures. Such adhesive mixtures exhibit a satisfactory peel and shear strength. Their heat-resistance property could, however, be improved on.

The task thus consisted in alleviating the disadvantages described above. The invention concerns a melt adhesive, basically consisting of a mixture of

A 100 parts by weight of at least one non-hydrated, linear block copolymerisate with the formula A-B-A that consists of

- a1) end-located non-elastomeric polymer blocks A consisting of monovinyl-aromatic monomers,
- a2) each of which having an average molecular weight of between 5,000 and 50,000 and
- a3) representing a percentage content of between 10 and 50% by weight in relation to the linear block copolymerisate A-B-A and where
- a4) B represents an elastomeric (co)-polymerisate consisting of butadiene and/or isoprene and in which case
- a5) the average molecular weight  $2A+B$  furthermore varies between 30,000 and 300,000;

B between 25 and 300% by weight of a resin with adhesive properties,

C between 5 and 200% by weight of a rubber diluent oil and, if required,

D other commonly used additives in effective quantities.

The melt adhesive is characterized by the fact that the elastomeric (co)-polymerisate a4) contains butadiene and isopropene in a weight ratio of between 70:30 and 5:95.

The component A to be used in accordance with the invention, i.e., the linear, rubberlike block copolymerisate A-B-A, forms the essential elastomeric component of the melt adhesive.

Monovinyl and monovinylidene-aromatic compounds that may be considered to structure the terminal-located non-elastomeric polymer blocks A consist of, for example, styrenes, the side-chain alkylated styrenes such as  $\alpha$ -methyl styrene and the nucleus-substituted styrenes such as vinyl toluene, ethyl vinyl benzene and others. The monovinyl and monovinylidene-aromatic compounds may also be used together in mixtures. However, it is preferred to use styrene alone.

In that regard, the block copolymerisate A-B-A generally contains between 10 and 50% by weight, particularly between 25 and 35% by weight, of monovinyl or monovinylidene-aromatic compounds and thus correspondingly between 90 and 50% by weight, preferably between 75 and 65% by weight, each in relation to the block copolymerisate A-B-A, of butadiene and isoprene that are polymerized into it. The intermediate part B of the block copolymerisate is a mixed polymerisate structured of butadiene and isoprene units, in which the weight ratio between butadiene and isoprene may vary over wide limits, e.g., 70:30 to 5:95. In this mixed polymerisate, the above-mentioned monomers may be present at random or in an arranged form as a function of the selected method of preparation. If the monomers are initially available in the form of a mixture for the manufacture to be described later, the anionic polymerisation is carried out without a polar solvent, thus producing a copolymerisate that can be described as a block copolymerisate with a lubricated transition, consisting of a first block part in which one monomer dominates, and a second block part in which the other monomers dominate. Statistical copolymerisates are formed with the use of polar solvents and the application of monomers; the same may be achieved with certain supply techniques.

The linear block copolymerisates A-B-A may be manufactured in a basically known manner with sequential polymerisation of the monomer in solution and in the presence of a monolithium hydrocarbon as the initiator and the subsequent bonding of the obtained active, living linear polymerisates with a bifunctional, reactive compound as the bonding agent. Monolithium hydrocarbons suitable as initiators are those with the general formula  $RLi$ , where R represents an aliphatic, cyclo-aliphatic, aromatic or mixed aliphatic-aromatic hydrocarbon residue with between 1 and 12 carbon atoms and represents in

particular an aliphatic hydrocarbon residue. Preferred are: n-, sec.-butyl lithium, isopropyl lithium and vinyl lithium, in which case the two substances mentioned first are particularly preferred.

The solvents used in the manufacture of the block copolymerisates may consist of inert, aliphatic, cyclo-aliphatic or aromatic hydrocarbons such as n-hexane, heptane, iso-octane, cyclohexane, cycloheptane, benzene, toluene and others. The polymerisation may be carried out with small quantities of polar solvents such as amines, alcoholates and ethers, particularly tetrahydrofuran. The polar solvents are generally used in quantities of between 0.05 and 10% by weight, preferably between 0.1 and 2% by weight, in relation to the weight of the total solvent. The polymerisation is carried out under the conditions commonly found in the anionic polymerisation with lithium-organic compounds such as an intergaseous environment with the exclusion of air and humidity. The polymerisation temperatures generally vary between 0 and 150 °C and are in a preferred manner selected between 20 and 100 °C.

To manufacture the linear block copolymerisates A-B-A, the monovinyl or monovinyl compounds are initially polymerized with the help of monolithium-hydrocarbon until the reaction is practically complete and to obtain the desired end-located, non-elastomeric polymer block -A-. A mixture of butadiene and isoprene, for example, is subsequently added to the solution of the resulting active living polymerisate, if need be with the addition of a polar solvent, thus achieving a statistical or non-statistical distribution of butadiene and isoprene at the active chain ends of the formed, living block polymerisate. The structuring of the intermediate part B of component A may, however, also be achieved with the known monomer supply techniques regarding the solution of the active living polymerisates. After the polymerisation but before the initiator's deactivation, a bifunctional reactive compound is added to the solution as a bonding agent to link the earlier formed active, linear block polymerisates  $A-B_{1/2}-Li$  at their terminal-located lithium-hydrocarbon bonds while forming a chemical link, thus forming a block copolymerisate A-B-A. Esters of acetic acid of alcohols with between 1 and 2 C atoms are used as the preferred bonding agents. The bifunctional bonding agent is generally added to the reaction solution in quantities that are equal to the quantity of

the initiator used. The bonding may be carried out at the same temperature as the polymerisation and is carried out at temperatures between 20 and 100 °C in a preferred manner.

The average molecular weight  $2xA+B$  of the rubberlike, linear block copolymerisate to be used in accordance with the invention (component A) should vary between 30,000 and 300,000. In that regard, each of the non-elastomeric polymer blocks A from the monovinyl or monovinylidene-aromatic compound generally has an average molecular weight of between 5,000 and 50,000, preferably between 15,000 and 25,000; the elastomeric copolymerisate B generally has an average molecular weight of between 20,000 and 200,000, preferably between 60,000 and 100,000. The molecular weights indicated are average viscosity values of the molecular weight.

For the melt adhesive mixture in accordance with the invention, it is possible to use the known substances of this type, described among others in the earlier mentioned documents, as the resins with adhesive properties (component B). To this group belong, for example, non-modified and modified colophonium, in which case multivalent esters of colophonium such as colophonium glycerine ester or colophonium penta erythrite ester are particularly favored.

Particularly preferred are the hydrated colophonium derivatives. Furthermore, it is also possible to use as resins with adhesive properties the known  $\alpha$  or  $\beta$  pinene resins with a molecular weight of between 100 and 2,000, as well as synthetic polyterpene resins and aliphatic diene-olefin hydrocarbon resins with a molecular weight of between 500 and 3,000. Cumaron-indene resins, polyindene resins and phenol-modified resins represent a further group of resins with adhesive properties. The molecular weight of these resins generally varies between 200 and 1,500. Furthermore, it is also possible to use the known resins based on styrene or the substituted styrenes with a low or average molecular weight such as between approximately 300 and 6,000 as the substances with adhesive properties. Examples thereof are: polystyrene resins, isobutylene/styrene copolymerisates and vinyl toluene/styrene copolymerisates. Polyisobutylene with a viscosimetric molecular weight of between 1,000 and 50,000 may also be considered as a substance with adhesive properties.



The resins with adhesive properties are used with a quantity of between 25 and 300% by weight, preferably between 50 and 150% by weight, for each 100% by weight of component A. The individual resins with adhesive properties may be used alone or in combination with others.

As a further component C, the melt adhesive mixture in accordance with the invention contains a rubber diluent oil in quantities of between 5 and 200% by weight for each 100% by weight of component A. In a preferred manner, between 10 and 100 parts by weight of the diluent oil are added for each 100 parts by weight of component A. In that respect, the term rubber diluent oil includes both the common diluent oils manufactured from petroleum fractions as well as olefin, oligomeric and low-molecular polymers and plant and animal oils and their derivatives. The petroleum fractions that can be used as diluent oils consist of mineral oils with a high boiling point and a controlled hydrocarbon composition and varying viscosities. They range from paraffinic to naphthenic to highly aromatic hydrocarbons. In a preferred manner, diluent oils consist of mineral oils that are produced from petroleum fractions and exhibit only a small percentage content of aromatic hydrocarbons. In a preferred manner, the percentage content of aromatic hydrocarbons should be less than 30% by weight, particularly less than 15% by weight, of the mineral oil. Considered particularly favorable is a composition, in which the mineral oil contains between 30 and 50% by weight naphthenic hydrocarbon, between 35 and 65% by weight paraffinic hydrocarbon and also aromatic hydrocarbon. The specific weights of the mineral oil (at 15 °C) range between approximately 0.80 and 1.00 g/ml, preferably between 0.83 and 0.91 g/ml; the viscosity generally varies between 10 and 100 cSt at 50 °C. The mineral oil boiling point is generally above 270 °C.

If required, commonly used additives D may be added to the melt adhesive mixture in accordance with the invention. This includes particularly anti-oxidants such as zinc dibutyl thiocarbamate, sterically hindered phenols, 2,5-di-tert.-amyl hydroquinone or chelate-forming phosphites; this also includes stabilizing agents, pigments, softeners, fillers or modifiers such as waxes, particularly paraffin waxes. The additives are added to the melt adhesive mixture in commonly used quantities. When using anti-oxidants, they are, for

example, added in quantities ranging between 0.1 and 3% by weight in relation to the melt adhesive mixture.

The melt adhesive mixture in accordance with the invention is manufactured by mixing the individual components. This may be carried out in a commonly known way and manner with the use of a solvent that must subsequently be removed, or in a preferred manner in the melt without using a solvent.

In a preferred manner, the mixing of the components in the melt is carried out at between 140 and 230 °C. It is preferred to prepare a part of the diluent oil or, in the event the formula contains little or no diluent oil, a part of the resins with the adhesive properties, if need be together with the anti-oxidants, and to subsequently add component A, i.e., the linear block copolymerisate, in a continuous manner. The remaining oil and/or resin is added as soon as the mixture has reached a homogenic state. To obtain mixing times that are as short as possible, it may be advantageous to pre-swell the linear block copolymerisate in the diluent oil before the mixing. It is also considered favorable to add the block copolymerisate in the form of particles that are as small as possible. Commonly known units such as kneaders, extruders or agitator tanks are used to mix the components.

The adhesive mixture in accordance with the invention may be applied in the melt and to suitable substrata with the help of commonly used melt adhesive application aggregates such as rollers or extruders or extrusion dies for flat sheets, such as the Bolten-Emerson system. Expensive solvent coating systems are thus not required in this case. The following are considered suitable substrata: plastic plates or plastic films, textiles made of synthetic or natural fibers, fleece, paper, wood, glass, metals, rubber, bituminous coatings, bitumen-coated cartons etc. The plastics indicated below are examples of suitable materials: polyolefins such as polyethylene or polypropylene, polyvinylchloride, polyethylene glycol terephthalate or polystyrene. The so-called transfer method is used to apply the adhesive mass to heat-sensitive films, i.e., the adhesive mass is initially applied in the form of a film to the silicon paper, which is subsequently, after cooling, transferred to the film.

The described melt adhesive mixtures are suited in particular for pressure-sensitive adhesives for the manufacture of self-adhesive materials such as self-adhesive films, self-adhesive labels, self-adhesive floor coverings, self-adhesive wall coverings, medicinal plasters and self-adhesive anti-droning materials.

The invention will be explained in the following with the help of examples and comparative tests. Unless indicated otherwise, the parts and percentage contents indicated refer to the weight. The given molecular weights were determined with the help of viscosity measurements carried out in an "Ubbelohde Capillary Viscosimeter".

Films with a thickness of 40  $\mu\text{m}$  and consisting of polyethylene glycol terephthalate are coated with a 25  $\mu\text{m}$  thick adhesive film in the following examples and comparative tests. The adhesive may be applied to the polyethylene glycol terephthalate in the form of a melt or solution (in toluene, for example). When using a solvent, it is necessary to evaporate the solvent under a reduced pressure. In that regard, the temperature of the coated film should not exceed approximately 130 °C. To evaluate the adhesive properties of the film coated with the adhesive, the surface adhesiveness is determined with the peel test carried out after the drying and at room temperature. Furthermore, the cohesion of the adhesive coating is determined with a shear test.

To carry out the peel test, 2 cm wide test strips are glued to a chrome-plated plate and peeled off in a direction parallel with the adhesive coating, i.e., at an angle of 180°, and the required force is measured thereafter. The peeling-off velocity is 300 mm/min. The measurement is carried out 24 hours after gluing.

The shear test is carried out in accordance with the method described in DT-OS 21 34 688. In that test, the test strips are glued to a highly-polished chrome-plated metal plate with the dimensions 20 x 25 mm. The coated metal plate is clamped in a vertical position. A 1000 g force is applied at the end of the adhesive strip and the time elapsed until the glue begins to come off

under the constant pulling force is measured. The measurement is carried out at temperatures of 23 °C and 50 °C.

Manufacture of a linear, non-hydrated A-B-A block copolymerisate:

360 g (3.46 mol) of a purified styrene are reacted in 4,670 g of cyclohexane with 18 m mol sec.-butyl lithium and polymerized for 1 hour at 60 °C in an inert gas environment until the reaction is practically complete. The molecular weight of the such obtained polystyrene was  $M_v = 20,000$  and was determined with the viscosimetric method. A mixture consisting of 280 g butadiene (5.19 mol) and 560 g isoprene (8.24 mol) was subsequently added over a period of 3 hours and at a temperature of between 60 and 90 °C. The bonding of the living polymers was achieved with the addition of 9 m mol acetic acid. Thus a block copolymer was obtained with  $M_v = 67,000$ . The polymerisate was precipitated by pouring the solution in alcohol and subsequently dried. The total styrene percentage content of the block copolymerisate was 30%.

#### Example 1

Manufacture of a melt adhesive mixture.

100 parts of the described linear block copolymerisate A-B-A were homogenized in a kneader and at mixing temperatures of approximately 200 °C with 50 parts of a naphthene-based diluent oil with a density of 0.902<sup>4</sup> (g/ml; 15 °C), an aromate content of 29%, a viscosity of 548 cSt at 20 °C and 67.8 cSt at 50 °C (Gatenex N 945 manufactured by Shell), 50 parts of a glycerine ester of hydrated colophonium (Foral 85), 50 parts of a synthetic polyterpene resin (Wing Tack 95) and 5 parts of an anti-oxidant (butylzimate). The individual steps were carried out such that resins and anti-oxidants were prepared first and that the block copolymerisates, initially swelled with the diluent oil, were added slowly. The obtained melt adhesive mixtures were tested as described above. The test results are summarized in the table, indicating values that were obtained with one melt adhesive mixture containing a three-block copolymerisate styrene/isoprene/styrene manufactured in accordance with the theory presented in (1).

### Comparative test

A styrene-isoprene-styrene three-block copolymerisate exhibiting a viscometrically determined molecular weight of  $M_v = 119,000$  and consisting of 16 parts styrene and 84 parts isoprene was used. This three-block copolymerisate was manufactured using the melt adhesive mixture formulation indicated in example 1. The values obtained for the peel and shear strengths, with the latter measured at 23 and 50 °C, are indicated in the following table.

Table

	Peel strength (N/2 cm)	Shear strength at 23 °C	in hours at 50 °C
Example	13.0 A	24	10
Comparative test	11.0 A	4 K	0.2 K

A = adhesion break

K = cohesion break

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